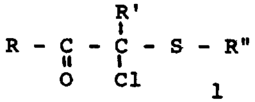
Tetrahedron Letters No.24, pp. 2089-2092, 1970. Pergamon Press. Printed in Great Britain.

THE CHEMISTRY OF SULFENYL CHLORIDES. CONDENSATION WITH 1,3,2-DIOXAPHOSPHOLENES TO FORM α-CHLORO-β-KETO SULFIDES.

David N. Harpp and P. Mathiaparanam[1]
Department of Chemistry
McGill University
Montreal, Canada.

(Received in UK 9 March 1970; received in UK for publication 27 April 1970)

The importance of α-chloro-β-keto sulfides (1) as useful intermediates



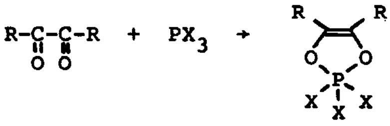
$$R-\underset{\underset{O}{\|}}{C}-\overset{\overset{R'}{|}}{\underset{\underset{Cl}{|}}{C}}-S-R''$$

1

in the syntheses of α-hydroxy acids, α-keto aldehydes, α-hydroxy aldehydes, methyl ketones, aldoses and a variety of heterocyclic compounds has been reported[2,3]. Two methods are available for their preparation: the decomposition of α-diazoketones with sulfenyl chlorides[4] and the action of thionyl chloride on β-keto sulfoxides[3]. In general these methods are useful for only a few members of the series and overall yields are somewhat low.

We wish to report a new condensation reaction whereby α-chloro-β-keto sulfides (1) can be prepared in high yield from readily available starting materials.

Trivalent phosphorus compounds are known to react with α-dicarbonyl derivatives to form 1:1 adducts. These adducts have been shown to be substituted 1,3,2-dioxaphospholenes (2)[5,6]. For example, benzil reacts with

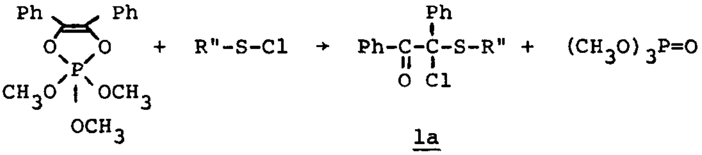


2

trimethylphosphite to form 2a ($R = C_6H_5$, $X = OCH_3$)[7] in quantitative yield.

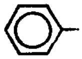
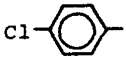
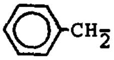
We have found that addition of sulfenyl chlorides to adduct 2a effects a rapid, exothermic condensation reaction giving α-chloro-β-keto-sulfides 1a (and trimethylphosphate). The results are summarized in Table I.

TABLE I



2a

1a

R"	mp of 1a[a] (°C)	yield %	NMR DATA τ
	118-120	80	2.10-3.20(14H,m),7.72(3H,s)
	113-115	82	2.10-3.00(m)
	122-124	83	2.10-3.00(m)
	109-110[b]	80	2.0-3.0(15H,m),6.15(2H,AB, J=12Hz)
CH_3CH_2	oil[b]	60	1.80-3.10(10H,m),7.30-7.90(2H,m), 8.60-9.20(3H,m)
$CH_3O_2CCH_2$	65-67[b]	75	1.90-2.65(10H,m),6.34(3H,s), 6.53(2H,AB,J=16Hz)
	135-136	93	1.80-2.90(m)

[a] Satisfactory elemental analyses were obtained for these compounds.

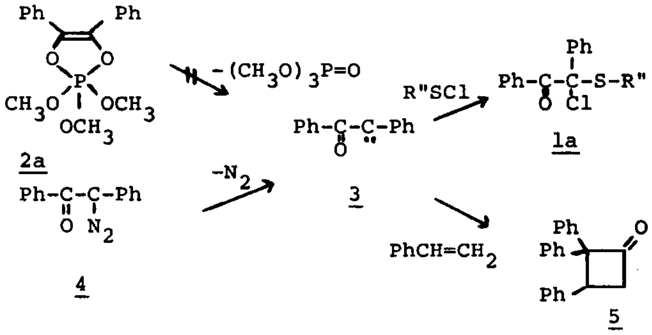
[b] Analyses were performed on the corresponding benzyloxy-keto-sulfides

In a typical experiment, trimethylphosphite (0.01 mole) was added to benzil (0.01 mole) under dry nitrogen. Once the exothermic reaction had subsided, the pale yellow syrup was dissolved in dry benzene (10 ml). A colorless solution was obtained and benzenesulfenyl chloride (0.01 mole) in benzene (10 ml) was added dropwise. As the addition continued, the deep red color of the sulfenyl chloride disappeared with the evolution of heat. Work up provided α-chloro-α-benzoylbenzyl-phenyl-sulfide in 82% yield.

The IR spectra of the chloro-keto-sulfides (1) showed a carbonyl band at 1685 cm^{-1}. The mass spectra generally revealed a weak parent ion M$^+$ along with (M-Cl)$^+$, $C_6H_5C \equiv O^+$(m/e 105) and R"S$^+$ as the major peaks[8]. The NMR data are summarized in Table I.

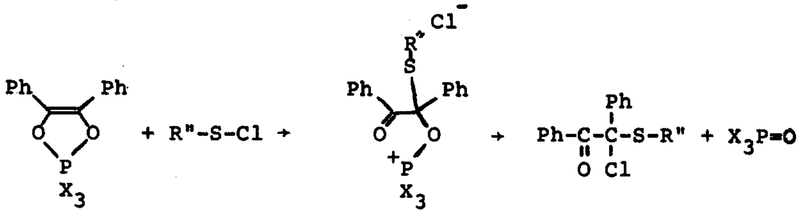
The condensation reaction proceeds in the dark and in the presence of a radical inhibitor (1,3,5-trinitrobenzene) with no appreciable change in the rate, indicating that a free radical mechanism is unlikely. The possibility of a carbene mechanism is also remote (Scheme I). While benzoylphenylcarbene 3 [9] (from azibenzil (4)) reacts with sulfenylhalide to give sulfide 1a (93%) such a carbene does not appear to be involved in the decomposition of the benzil-trimethyl phosphite adduct 2. No 2,2,3-triphenylcyclobutanone (5) was formed on treatment of adduct 2 with styrene whereas azibenzil (4) gave (5) under identical conditions[10].

Scheme I



Thus, an ionic mechanism appears likely (Scheme II). Experiments are in progress to determine the mechanism and to extend the scope of the condensation reaction.

Scheme II



2a X = $-OCH_3$

1a

REFERENCES

(1) N.R.C.C. Scholar 1967-70.

(2) (a) F. Weygand and H.J. Bestmann, *Angew. Chem.*, **72**, 525 (1960); *Acta Chim. Hung. Tomus.*, **18**, 59 (1959); (b) F. Weygand, H.J. Bestmann, H. Zeimann and E. Klieger, *Chem. Ber.*, **91**, 1043 (1958) and references cited therein.

(3) G.A. Russell and L.A. Ochrymowycz, *J. Org. Chem.* **34**, 3618 (1969).

(4) F. Weygand and H.J. Bestmann, *Z. Naturforsch* **10b**, 296 (1955).

(5) (a) L.D. Quinn, pp. 83-96, G. Pfundt and G.O. Schenk, pp. 379-388 in "1,4 Cycloaddition Reactions" Edit. by J. Hamer; Academic Press, New York, N.Y. (1967); (b) F. Ramirez, *Pure and Applied Chemistry*, **9**, 337 (1964); *Bull. Soc. Chim. France*, 2443 (1966), *Acc. Chem. Res.* **1**, 168 (1968); (c) F. Ramirez, S.L. Glaser, A.J. Bigler and J.F. Pilot, *J. Amer. Chem. Soc.* **91**, 496 (1969); (d) F. Ramirez, A.V. Patwardhan, H.J. Kugler and C.P. Smith, *Tetrahedron Letters*, 3053 (1966).

(6) Some adducts of $(Me_2N)_3P$ exist in the phosphonium enolate form (ref. 5d).

(7) The 1:1 adduct obtained from benzil and trimethylphosphite is named 2,2-dihydro-4,5-diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphospholene.

(8) A detailed study of the fragmentation pattern of the α-chloro-β-keto sulfides is in progress.

(9) W. Kirmse in "Carbene Chemistry" pp.118-119; Academic Press, New York, N.Y. (1964).

(10) C.S. Marvel and M.I. Kohan, *J. Org. Chem.* **16**, 741 (1951).

ACKNOWLEDGEMENT. We wish to thank the National Research Council of Canada for financial support of this work.